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THE UPPER ATMOSPHERE,
Part 1 of an Examination of the Application
to Satellite Meteorology of Various Segments
of the Electromagnetic Spectrum

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ULTRAVIOLET SPECTROSCOPY OF
THE UPPER ATMOSPHERE
(Part 1 of an Examination of the Application
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R. O. Hundley

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PREFACE

The RAND Corporation is currently engaged in a program of research on Satellite Meteorology under NASA Contract NASr-21(0/). As part of the program studying the scientific utilization of meteorological satellite data and the implications of new techniques and measurements to meteorological satellite development, RAND is examining the entire electromagnetic spectrum to determine how each spectral region can best be used for meteorological purposes. This Memorandum, one chapter of the study, covers the middle ultraviolet and vacuum ultraviolet region.

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SUMMARYover
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This Memorandum surveys the middle and vacuum ultraviolet spectroscopy of the upper atmosphere. The various physical and chemical processes involved in the interaction of radiation with the atoms and molecules of the upper atmosphere are reviewed. These processes include radiation absorption processes, such as photodissociation, photoionization, and resonance absorption; radiation scattering processes, such as Rayleigh scattering and resonance scattering; and radiation emission processes, such as chemiluminescence. The ultraviolet spectral features that result from these processes are summarized. These features include molecular absorption and emission bands, discrete atomic spectral lines, and atomic and molecular absorption continua. Various ways are discussed in which rocket and satellite observations of these spectral features can be used to study the composition of the upper atmosphere. These ways include observations of the absorption of radiation by the upper atmosphere, observations of the scattering of solar radiation by the upper atmosphere, and observations of the emission of ultraviolet radiation from the upper atmosphere. As an example of one of the many spectroscopic techniques discussed in the Memorandum, observations of the solar spectrum in the region from 1000 \AA to 2000 \AA , made from a rocket rising through the atmosphere, can be used to determine the molecular oxygen concentration as a function of altitude. As another example, satellite observations of the amount of solar radiation reflected from the atmosphere at 1302 \AA , 1305 \AA , and 1306 \AA can be used to determine the atomic oxygen concentration in the upper atmosphere. These are but two examples

Author

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of the many spectroscopic techniques discussed in the Memorandum. Using a variety of these techniques, it should be possible to add greatly to our knowledge of the distribution of the atomic and molecular constituents of the upper atmosphere. *Author*

ACKNOWLEDGMENTS

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I. INTRODUCTION

The advent of rockets and satellites opens up a new region of the electromagnetic spectrum for use in studying the earth's upper atmosphere. This new region is the middle and vacuum ultraviolet--the region of wavelengths shorter than 3000 \AA . This spectral region is of great interest for upper atmospheric research, since in it occur the most important spectral features of several of the upper atmospheric constituents, such as O , N , O^+ , N^+ , O_2^+ and NO^+ . At the present time our knowledge of the distribution of these constituents in the upper atmosphere is very limited, and ultraviolet observations from rockets and satellites may provide a vast increase in our knowledge.

In this Memorandum we will discuss briefly the important ultraviolet radiation processes that occur in the upper atmosphere, and the general spectral features of the ultraviolet radiation that result from these processes. In addition, we will discuss ways in which observations of the various spectral features can be used to study the distribution of the atomic and molecular constituents of the upper atmosphere.

At this point it must be emphasized that satellite observations of the atmosphere in the middle and vacuum ultraviolet will be, of necessity, limited to studies of the upper atmosphere. This is because radiation of wavelengths shorter than 3000 \AA is strongly absorbed by the various atmospheric constituents. In the 2000 \AA to 3000 \AA region, for example, satellite observations will be limited to the region above

the ozone layer, which has its maximum at about 30 km. In the 1000 \AA ⁰ to 1800 \AA ⁰ region the satellite observations will be limited to the region above about 100 km due in large part to O_2 absorption, and at shorter wavelengths the lowest accessible altitude will be even higher.

Although the kinds of satellite observations dealt with in this Memorandum relate primarily to upper atmosphere composition, these observations can almost certainly be related to a broader set of interacting phenomena in the atmosphere. It is clear, for example, that the distribution of ozone is determined to a large extent by horizontal advection of air in the 15 to 30 km region from ozone source regions, that atomic/molecular oxygen ratios in the 80 to 100 km region of O_2 dissociation are affected by vertical as well as horizontal air motions; and that, in turn, compositions at heights above 100 km are affected by changes at 100 km due to molecular transport (diffusion) in the vertical. There are many other examples. More generally, changes in distribution of atomic and molecular constituents in the upper atmosphere may be significant and useful indicators of dynamic changes in motion and energy balance in the atmosphere as a whole, and therefore they should be treated in as broad a context as possible after the observations have been made.

This survey of the middle and vacuum ultraviolet will begin in Section II with a discussion of the various physical processes occurring in the upper atmosphere which are important in determining the details of the ultraviolet spectrum as observed from a rocket or satellite. Section III gives a general survey of the spectral features that result from these processes, and Section IV discusses various ways in which

rocket and satellite observations of these spectral features can be used to study the composition of the upper atmosphere. Finally, in Section V we discuss briefly some of the ultraviolet observations of the upper atmosphere that have been carried out already from rockets and satellites.

II. IMPORTANT RADIATION PROCESSES

Due to the low particle densities in the upper atmosphere, collisions are not sufficiently frequent to establish a thermal equilibrium distribution, in so far as the internal energy states of the atoms and molecules are concerned. Because of this, the ultraviolet radiation properties of the upper atmosphere cannot be obtained simply by consideration of the Planck radiation function, as would be the case for the IR radiation from the lower atmosphere, for example, but instead a detailed consideration must be made of the various physical processes involved in the interaction of radiation with the atoms and molecules of the upper atmosphere.

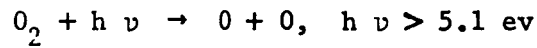
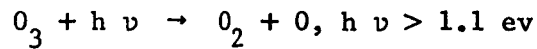
These physical processes may be grouped in three categories:

(A) Radiation absorption processes, which determine the depth to which the solar ultraviolet radiation penetrates into the atmosphere, and also the depth to which a UV satellite may "see" into the atmosphere; (B) Radiation scattering processes, which determine the amount of solar ultraviolet radiation reflected by the upper atmosphere; (C) Radiation emission processes, which determine the amount of ultraviolet radiation emitted by the upper atmosphere. In the remainder of this section we will briefly review these three types of physical processes and their effect on the ultraviolet radiation properties of the upper atmosphere.

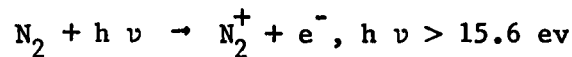
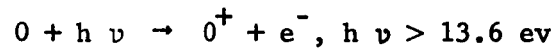
RADIATION ABSORPTION PROCESSES

The most important radiation absorption processes in the upper atmosphere are those of continuous absorption. These are of two general types: molecular dissociation, examples of which are

0.2×10^{-10} ergs
 1.602×10^{-12} ergs



where $h\nu$ is the photon energy; and atomic or molecular ionization, examples of which are



These continuous absorption processes are characterized by an absorption cross section σ_ν , which in general is a slowly varying function of the frequency ν . The decrease in radiant intensity of monochromatic radiation due to a continuous absorption process is given by Beer's law

$$I_\nu = I_{0\nu} e^{-\tau_\nu}$$

where $I_{0\nu}$ is the intensity of the incident radiation, and I_ν is the intensity of the radiation after having penetrated an optical depth τ_ν . The optical depth is related to the actual optical path length ℓ in the atmosphere by

$$\tau_\nu = \int_0^\ell \sigma_\nu N(\ell') d\ell'$$

where $N(\ell')$ is the particle density of the absorbing species as a function of position along the optical path.

The value of the absorption cross section depends on the particular atomic or molecular species involved and on the frequency. In general the continuous absorption cross sections for atmospheric gases have values between 10^{-17} cm^2 and 10^{-23} cm^2 . The review article by Watanabe⁽¹⁾ gives a detailed discussion of the values of the absorption cross sections of the atmospheric gases.*

These continuous absorption processes are of fundamental importance in ultraviolet studies of the atmosphere because they determine the depth to which the solar ultraviolet radiation may penetrate into the atmosphere, and also the depth to which a UV satellite may see into the atmosphere. As an illustration of this, consider the altitude at which the intensity of solar radiation at vertical incidence will be reduced by a factor of e . This will be the altitude z of unit optical depth in the atmosphere, which is given by

$$\sigma_v \int_z^{\infty} N(z') dz' = 1$$

where $N(z')$ is now the particle density of the absorbing species as a function of altitude. Figure 1, based on Allen's tables,⁽²⁾ is a plot of this altitude of unit optical depth. The absorption above 2000 \AA is principally due to ozone, between 850 and 2000 \AA to molecular oxygen, and below 850 \AA to all constituents.

In addition to the continuous absorption processes discussed above, resonance absorption in atomic lines or molecular bands will also occur in the upper atmosphere. By this is meant absorption processes of the form

* In Section III we briefly review the values and frequency dependence of the absorption cross section of the atmospheric gases.

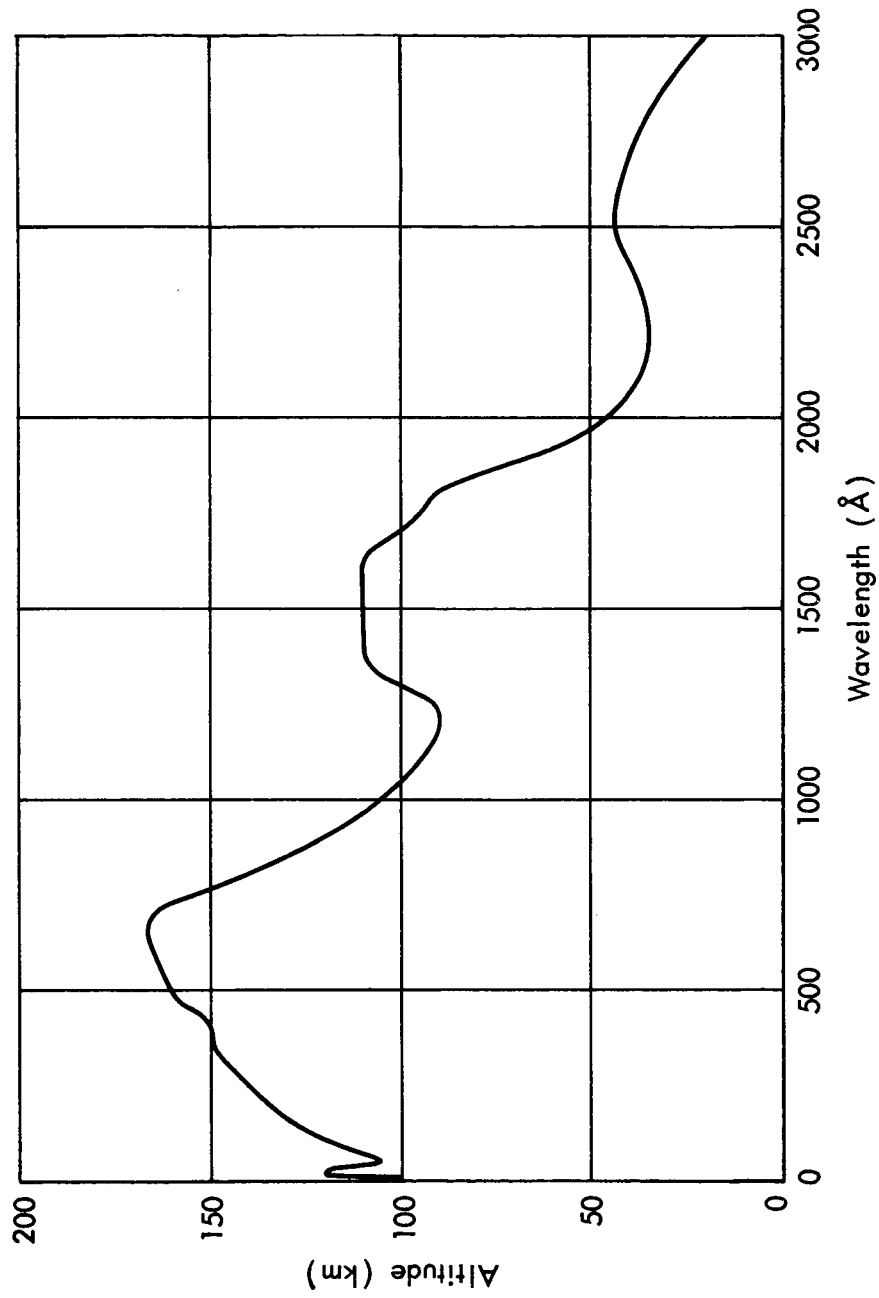
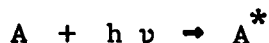


Fig. 1 — Penetration of solar ultraviolet radiation



where A and A^* denote quantum states of some atom or molecule. In order for such a resonance absorption process to occur, the photon energy $h\nu$ must be almost exactly equal to the energy difference between the two quantum states. Because of this, the absorption cross section for a resonance transition is a very rapidly varying function of frequency; it is essentially zero except in a very narrow spectral region, where it can attain relatively large values.

The strength of a resonance absorption transition is characterized by the oscillator strength f . This is related to the absorption cross section σ_ν by

$$\int \sigma_\nu d\nu = \frac{\pi e^2}{mc} f$$

where e is the electronic charge, m the electronic mass, c the speed of light, and the integral extends over the entire absorption line.* The value of f will depend on the details of the particular transition. For the strongest atomic absorption lines, $f \sim 1$. For transitions which are partially forbidden by quantum mechanical selection rules, f can be much lower, 10^{-6} or less. For detailed tables of atomic oscillator strengths, see Ref. 2.

The actual value of the absorption cross section will also depend on the shape and width of the absorption line. For the physical conditions occurring in the upper atmosphere, the line shape and width are determined primarily by Doppler broadening, due to the random thermal

* $\pi e^2/mc = 2.65 \times 10^{-2} \text{ cm}^2/\text{sec}$

motions of the atoms and molecules, and natural line broadening, due to the finite lifetimes of atomic and molecular energy levels.* The magnitude of the Doppler broadening is determined by the Doppler width $\Delta\nu_D$, given by

$$\Delta\nu_D = \frac{\nu_0}{c} \left(\frac{2KT}{M} \right)^{1/2}$$

where K is Boltzmann's constant, T the temperature, M the mass of the atom or molecule involved, and ν_0 the central frequency of the absorption line. Typical values of $\Delta\nu_D$ for ultraviolet absorption lines in the upper atmosphere will be 10^9 to 10^{10} sec^{-1} . The magnitude of the natural line broadening is determined by the natural line width $\gamma = \gamma_1 + \gamma_2$, where γ_1 and γ_2 are the decay rates of the two quantum states involved in the absorption process. For the strongest atomic absorption lines $\gamma \sim 10^8 \text{ sec}^{-1}$; for partially forbidden lines γ is much smaller than this.

We see that in the upper atmosphere $\gamma/\Delta\nu_D \ll 1$. Under these conditions the Doppler broadening will determine the shape of the central region of the absorption line. The absorption cross section in this region will be given by

$$\sigma_\nu = \sigma_0 e^{-(\nu - \nu_0)^2 / (\Delta\nu_D)^2}$$

where σ_0 , the peak value of the cross section, is given by

* Line broadening due to collisions (pressure broadening) will not be important above about 50 km, due to the low collision frequencies at high altitudes.

$$\sigma_o = \frac{\pi^{1/2} e^2 f}{mc \Delta v_D}$$

The above expression for the cross section is correct for $(\nu - \nu_o)^2 \lesssim (\Delta \nu_D)^2$, the central region of the line. Far out on the wings of the line, where $(\nu - \nu_o)^2 \gg (\Delta \nu_D)^2$, the line shape will be determined by the natural line broadening, and the cross section will be

$$\sigma_\nu = \frac{e^2 f}{4\pi mc} \cdot \frac{\gamma}{(\nu - \nu_o)^2}$$

In the intermediate region, between the line center and the wings, the line shape is determined by a combination of Doppler and natural broadening, and the resulting expression for the cross section is more complicated. Reference 3 provides a discussion of the cross section in this region.

The above expressions show that the absorption cross section due to a resonance transition will be very small except in a region approximately $\Delta \nu_D$ wide about the central frequency. As noted above, typical values of $\Delta \nu_D$ for UV absorption lines in the upper atmosphere will be 10^9 to 10^{10} sec^{-1} , or in wavelength units, 10^{-2} to 10^{-3} \AA . For the strongest transitions, with $f \sim 1$, this gives peak absorption cross sections of the order of 10^{-12} cm^2 . This is much larger than the strongest continuous absorption cross sections. However, because these large values of cross section are limited to such very narrow wavelength regions, the resonance absorption processes

are of less importance in the photochemistry of the upper atmosphere than are the continuous absorption processes. However, as pointed out in Section IV, they can still be important for diagnostic purposes.

The width of a resonance absorption line, 10^{-2} to 10^{-3} Å, will generally be much less than the spectral resolution of the experimental equipment. Because of this, the measured intensity I will not obey Beer's law, but rather an expression of the form

$$I = I_0 \int e^{-\int_0^L \sigma_\nu N(l') dl'} d\nu$$

where the frequency integral extends over the entire absorption line.

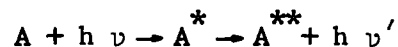
RADIATION SCATTERING PROCESSES

There are two types of radiation scattering phenomena that are important in the upper atmosphere: Rayleigh scattering, and resonance or fluorescent scattering. Rayleigh scattering is the scattering of light by bound atomic or molecular electrons. The Rayleigh scattering cross section is a slowly varying function of frequency, and is of the order of 10^{-25} cm^2 in the ultraviolet. Tables of the Rayleigh scattering cross section down to 2000 Å have been given by Penndorf.⁽⁴⁾

Resonance and fluorescent scattering also involve the scattering of light by atoms or molecules. However, for these phenomena the radiation frequency must correspond to the energy difference between two of the quantum states of the atom or molecule. For resonance scattering the initial and final quantum states are the same, and the scattered radiation is of the same frequency as the incident radiation; i.e.,



For fluorescent scattering the initial and final quantum states are different, and the scattered radiation is of a different frequency, i.e.,



Resonance and fluorescent scattering are very closely related to the process of resonance absorption ($A + h\nu \rightarrow A^*$) discussed previously. For a given spectral line, the resonance scattering cross section $\sigma_{\text{Res}}(\nu)$ will be given in terms of the resonance absorption cross section σ_ν by (5)

$$\sigma_{\text{Res}}(\nu) = \sigma_\nu FR$$

where F describes the effects of collision deactivation, and R is the branching ratio for the re-emission of the radiation. The coefficient F represents the fraction of excited atoms (A^*) which are not collisionally deactivated before they can re-radiate. It is given by

$$F = \frac{\Gamma}{\Gamma + \gamma_c}$$

where Γ is the total radiative decay rate of the excited state A^* , and γ_c is the rate of collisional deactivation. The value of F depends on the spectral line involved, but for the strongest atomic lines $\gamma_c/\Gamma \ll 1$ for altitudes above about 50 km, so that $F \approx 1$ and collisional deactivation is unimportant. For weak, partially forbidden lines, however, collisional deactivation can be important to much

higher altitudes, 100 km or higher. For a further discussion of collisional deactivation, see Ref. 5.

The branching ratio R for resonance scattering represents the fraction of the re-emitted radiation which is in the same spectral line as the absorbed radiation. The value of R depends on the spectral line involved, but for resonance scattering in the vacuum ultraviolet it is generally not far from unity. The branching ratio R for fluorescent scattering is defined similarly; it represents the fraction of the re-emitted radiation which is in the particular fluorescent line in question.

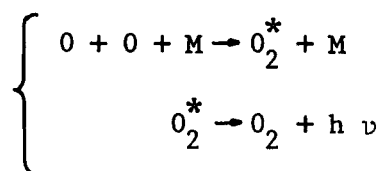
As the above discussion shows, subject to corrections introduced by collisional deactivation and radiative branching, the resonance or fluorescent scattering cross section will have the same magnitude and frequency dependence as the resonance absorption cross section. Resonance and fluorescent scattering phenomena will therefore have two of the characteristic features of resonance absorption: large values of cross section (as large as 10^{-12} cm^2) limited to very narrow spectral regions (10^{-2} to 10^{-3} \AA).

These radiation scattering processes (Rayleigh, resonance, and fluorescent scattering) are very important in ultraviolet studies of the atmosphere, because in conjunction with the absorption processes they determine the amount of solar ultraviolet radiation that is reflected by the upper atmosphere, i.e., the ultraviolet albedo of the earth. Because the continuous absorption cross sections are so much larger than the Rayleigh scattering cross section, the ultraviolet albedo will be generally small, of the order of 10^{-3} or

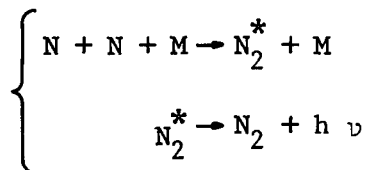
less. The only exceptions to this rule will occur for wavelengths corresponding to strong resonance scattering lines, where the albedo may approach unity.

RADIATION EMISSION PROCESSES

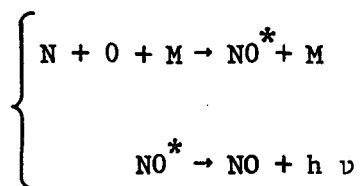
There are a number of chemical reactions occurring in the upper atmosphere which may produce radiation in the middle and vacuum ultraviolet. One example of these, which has already been observed in the night airglow, is the three-body recombination of atomic oxygen



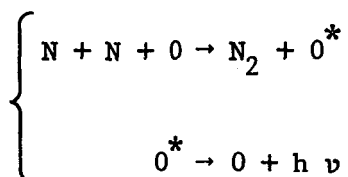
which produces the Herzberg bands of O_2 in the region from 2600 Å to 4300 Å.⁽⁵⁾ Other three-body recombination processes which may contribute to the ultraviolet emission from the upper atmosphere include



which may produce the Vegard-Kaplan and Lyman-Birge-Hopfield bands of N_2 , and

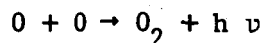


which may produce the β , γ , and δ bands of NO. Another example of a radiation-producing reaction is

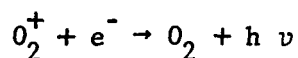


which is known to produce the 5577 Å line of atomic oxygen in the night airglow, and should also produce an oxygen line at 2972 Å.

In addition to the above reactions, there also exists the possibility of radiative recombination reactions, such as



or



or



The amount of ultraviolet emission in the upper atmosphere from these and other chemiluminescent reactions will depend on the concentrations of the reacting species, and on the rate constants for the chemical reactions. Unfortunately, our knowledge of the rate constants for chemiluminescent reactions is very meager, so that at the present time it is not possible to make accurate predictions for the ultraviolet

emission in the upper atmosphere due to photochemical processes. For a discussion of the current state of knowledge concerning photochemical reactions in the upper atmosphere, the reader is referred to Chamberlain⁽⁵⁾ and Cadle.⁽⁶⁾

Another possible source of ultraviolet radiation is collisional excitation of atoms or molecules, followed by radiative de-excitation. This process will be limited by the effects of collisional de-excitation, and also by the available excitation energy. Because of the low collision frequencies in the upper atmosphere, collisional de-excitation will not be important above about 50 km, unless the particular radiative de-excitation process is partially forbidden by selection rules. The amount of available excitation energy will be a much more serious limitation however, since the middle and vacuum ultraviolet require excitation energies of 4 ev or more. The kinetic temperature in the upper atmosphere is only of the order of 0.1 ev or less, so that excitation of ultraviolet radiation by the collision of ambient air atoms or molecules should be negligible. However, in auroral regions, where the atmosphere is bombarded by high energy particles, there should be sufficient energy available to collisionally excite the middle and vacuum ultraviolet.

III. SURVEY OF SPECTRAL FEATURES

In this section we wish to briefly discuss the most prominent ultraviolet spectral features of the atomic and molecular constituents of the upper atmosphere. We will first consider the molecular constituents, and then the atomic constituents.*

MOLECULAR SPECTRA

1. O_3 . For the purpose of the present discussion, the spectral region to be considered begins with the absorption bands of ozone. The Huggins bands, the first group of these, extend from 3600 \AA to 3200 \AA . These bands are weak, with a cross section of about 10^{-20} cm^2 , and produce only slight absorption of the solar radiation. The strong ozone absorption and the strong attenuation of solar radiation begins with the Hartley bands. These bands start at about 3200 \AA , and extend down to about 2340 \AA . At this point a dissociation continuum begins which extends down to 2100 \AA . At the peak of the Hartley bands, near 2600 \AA , the absorption cross section is about 10^{-17} cm^2 .

Ozone has several other absorption bands and continua in the region below 2100 \AA . They do not play an important role in atmospheric phenomena, however, since radiation in this spectral region is absorbed higher in the atmosphere by the O_2 .

2. O_2 . The ultraviolet spectrum of O_2 begins with the Herzberg bands, which occupy the region from about 4300 \AA down to 2400 \AA , where a dissociation continuum begins, which extends to about 1925 \AA . The Herzberg bands and continuum are very weak, with an absorption cross section of the order of 10^{-23} cm^2 . At about 1925 \AA the strong Schumann-

*For a more complete discussion of the ultraviolet spectral features of the atomic and molecular constituents of the upper atmosphere, the reader is referred to Herzberg (Refs. 7 and 8) and the review article by Watanabe (Ref. 1) from which the material in this section has been abstracted.

Runge band system begins, extending to 1752 \AA , where the Schumann-Runge dissociation continuum begins. This extends to about 1300 \AA , and at its peak, near 1425 \AA , the absorption cross section is approximately $1.5 \times 10^{-17} \text{ cm}^2$.

In the region between 1025 \AA and 1300 \AA , O_2 has a very complicated, and as yet unclassified, band spectrum, with the cross section varying rapidly between 10^{-17} and 10^{-20} cm^2 . The ionization continuum of O_2 begins at 1026.5 \AA and extends down to about 100 \AA . It peaks in the region between 400 \AA and 600 \AA , where the cross section is about $3 \times 10^{-17} \text{ cm}^2$. Superimposed on this continuum are a number of band systems. The most important of these, the Hopfield bands, lie between 850 \AA and 1050 \AA . They are the strongest bands of molecular oxygen, and have a peak cross section of $5 \times 10^{-17} \text{ cm}^2$.

3. N_2 . The ultraviolet spectrum of N_2 begins at about 1450 \AA with a series of discrete bands, the Lyman-Birge-Hopfield bands, which extend down to about 1000 \AA . These bands are very narrow, and have maximum absorption cross sections of the order of 10^{-20} cm^2 . Between the L-B-H bands, the cross section is much lower, of the order of 10^{-23} cm^2 .

In the region between 800 \AA and 1000 \AA the N_2 spectrum is extremely complicated, with several band systems. The cross section in this region varies rapidly between 10^{-17} and 10^{-19} cm^2 . The ionization continuum of N_2 begins at 800 \AA and extends down to at least 200 \AA . The absorption cross section in this region is about 10^{-17} cm^2 .

It is interesting to note that there are no known dissociation continua of N_2 .

4. NO. Nitric oxide is only a trace constituent of the upper atmosphere. However, it is expected to play an important role in the formation of the ionosphere, and for this reason it is interesting to study its distribution in the upper atmosphere.

The ultraviolet absorption spectrum of NO begins at about 2300 Å. From there down to 1340 Å there are a number of strong bands, the so-called $\beta, \gamma, \delta, \epsilon, \beta',$ and γ' bands. The ionization continuum begins at 1340 Å, and in the spectral region from 1000 Å to 1340 Å the absorption cross section is of the order of 10^{-18} cm^2 . Below 1000 Å it increases to about 10^{-17} cm^2 .

5. Ionized Molecular Constituents. The most important ionized molecular constituents of the upper atmosphere are O_2^+ , N_2^+ , and NO^+ . Because of their low concentration compared to the neutrals, they will not contribute significantly to the absorption spectra of the atmosphere. However it may be possible to observe their spectra in emission or resonance scattering.

The most prominent vacuum ultraviolet spectra of these molecules are: O_2^+ , the second negative bands in the region around 2500 Å; N_2^+ , the second negative bands in the region around 2000 Å*; and NO^+ , the Miescher-Baer bands in the region around 1400 Å.

6. Other Molecular Constituents. There are a number of other minor molecular constituents of the atmosphere for which vacuum ultraviolet observations from satellites may have useful application. These include H_2O , CO_2 , NO_2 , and OH. For a description of their spectra, and

*The first negative bands of N_2^+ , which occur between 3500 Å and 5000 Å, have been observed in the aurora and airglow.

for further details concerning the molecular spectra discussed above, the reader is referred to Watanabe's article.⁽¹⁾

Figure 2 summarizes this section and presents a chart of the most prominent molecular spectral features.

ATOMIC SPECTRA

The spectra of the atomic constituents of the upper atmosphere are much simpler than the molecular spectra. The spectrum of a particular atomic constituent will consist of a series of discrete spectral lines plus an ionization continuum. Table 1 shows some of the most important ultraviolet spectral lines of the atomic constituents of the upper atmosphere. We include in this table atomic oxygen and nitrogen, and also atomic hydrogen and helium, which become the dominant atomic species in the extreme upper atmosphere. We also include O^+ and N^+ , which are important in the ionosphere, and He^+ , which may occur in the extreme upper atmosphere.* The table also shows the peak absorption cross sections σ_0 associated with the various spectral lines. These cross sections have been calculated using the formulas given in Section II, together with the f values of Allen,⁽²⁾ and assuming a temperature of 300° Kelvin.

In so far as upper atmospheric phenomena are concerned, the only important atomic absorption continua will be the ionization continua of O and N. The ionization continuum of O begins at 910 Å and peaks at about 540 Å, where the absorption cross section is about 10^{-17} cm^2 . At shorter wavelengths the cross section slowly decreases. The ionization continuum of N begins at 850 Å and peaks at about 650 Å, where the cross section is also about 10^{-17} cm^2 .

*In the table we use the following conventional notation: OI denotes neutral oxygen, OII denotes singly ionized oxygen, etc.

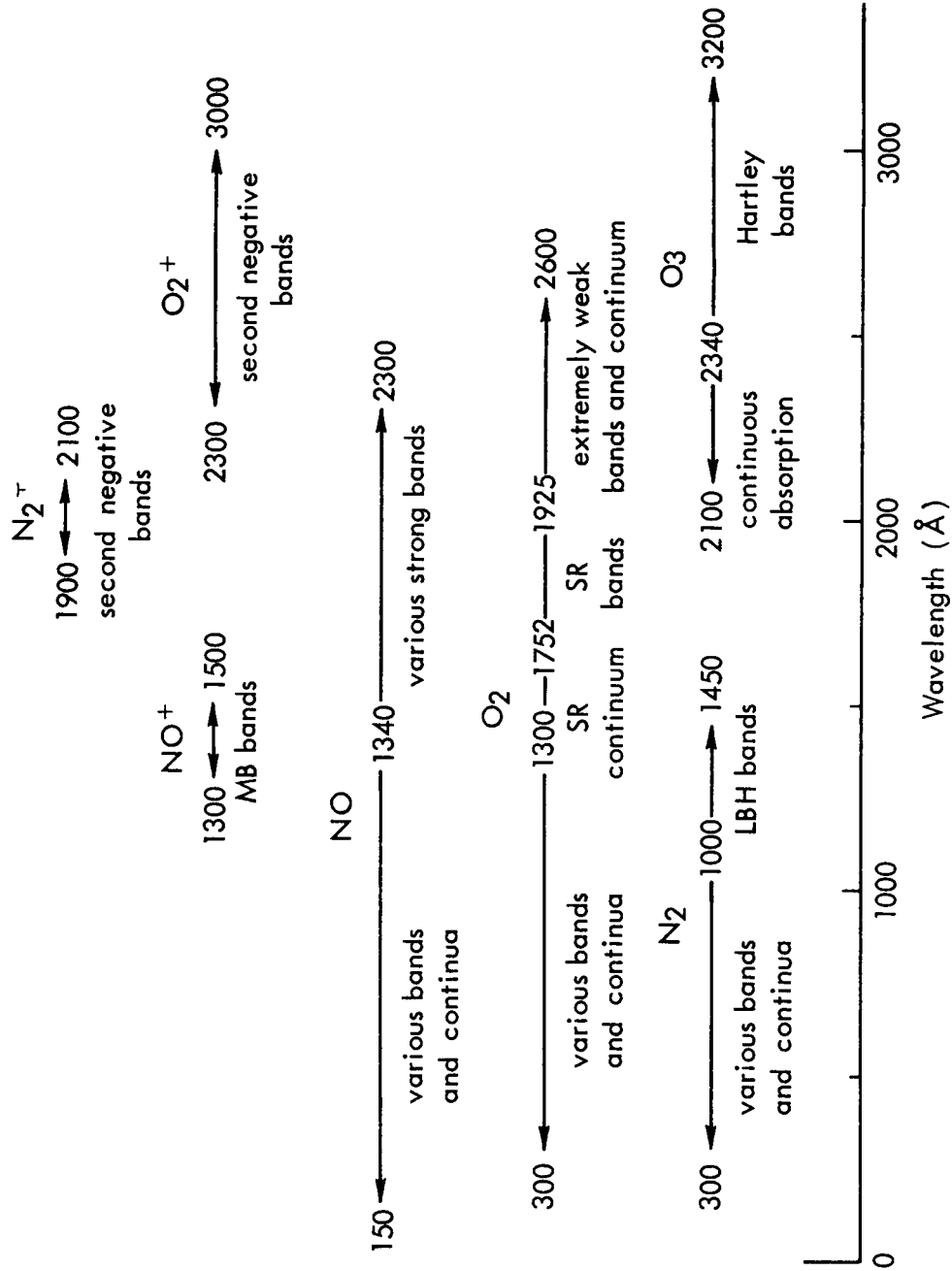


Fig. 2 — Molecular spectral features

Table 1
ATOMIC SPECTRAL LINES

Wavelength (\AA)	Species	$\sigma_0 (10^{-12} \text{ cm}^2)$
304	He II	0.25
584	He I	0.40
832.8	O II	0.41
833.3		0.82
834.5		1.2
1084.0	N II	1.5
1084.6		1.5
1085.5		0.24
1085.6		1.3
1134.2	N I	0.52
1134.4		1.0
1135.0		1.5
1199.6	N I	0.30
1200.2		0.20
1200.7		0.10
1215.7	H I	0.50
1302.2	O I	0.23
1304.9		0.23
1306.0		0.23
1355.6	O I	2.2×10^{-6}
1358.5		1.1×10^{-6}

IV. SPECTROSCOPIC TECHNIQUES FOR STUDYING ATOMIC AND MOLECULAR CONSTITUENTS OF THE UPPER ATMOSPHERE

This section will discuss various ways in which observations of the middle and vacuum ultraviolet spectra of the earth's atmosphere may be used to study the composition of the upper atmosphere. The spectroscopic techniques discussed here are not new or unusual, and their application to the study of the upper atmosphere is not original. Indeed, there have already been rocket and satellite observations conducted utilizing some of these techniques.*

This section is not intended to be a comprehensive discussion of all the possible spectroscopic techniques for studying the upper atmosphere from a satellite. It is merely a discussion of certain techniques which have been proposed recently. It may well be that further study of this subject will suggest other techniques with greater usefulness than these.

The spectroscopic observations to be discussed here fall into three categories: absorption observations, resonance scattering observations, and emission observations.

ABSORPTION OBSERVATIONS

An absorption experiment basically involves observing a radiation source through an intervening mass of absorbing gas. For vacuum ultraviolet studies of the upper atmosphere this cannot be done from the ground, but may be accomplished in various ways, such as:

*These previous observations are reviewed in Section V.

- (1) Observing the sun from a rocket or satellite passing through the upper atmosphere. This will permit a study of that part of the atmosphere above the rocket or satellite.
- (2) Observing the setting or rising sun from a satellite above the atmosphere. This will permit a study of the twilight atmospheric conditions.
- (3) Observing the occultation of a star by the earth's atmosphere. This is similar to the preceding technique, but will not be limited to a study of twilight conditions.
- (4) Use of two satellites, one of them carrying a strong ultraviolet source.

The basic features of the absorption experiment will be the same, no matter which of the above techniques is used. In the discussion below the basic features will be emphasized, not the particular experimental technique.

There are two basic types of absorption experiments: absorption by a molecular or atomic continuum, and absorption by an atomic spectral line or a narrow molecular spectral feature. The precise difference between the two cases is that in the first case the absorption cross section is essentially constant across the sensitive spectral range of the experimental equipment, whereas in the second case the absorption cross section is rapidly varying across this spectral range. Because of this difference, the analysis of the absorption measurements is distinctly different in the two cases.

The case of continuous absorption has been briefly discussed in Section II. As indicated there, the decrease in radiant intensity due to a continuous absorption process is given by Beer's law, which may now be written as

$$I_{\nu} = I_{0\nu} e^{-\sigma_{\nu} \eta}$$

where $I_{0\nu}$ is the source intensity, I_{ν} is the residual intensity after absorption, σ_{ν} is the absorption cross section, and η is given by

$$\eta = \int N(x) dx$$

where $N(x)$ is the density of the absorbing species, and the integral extends along the line of sight from the source to the detector.

It may be seen that the absorption measurement determines η , the total number of absorbing atoms (or molecules) per unit area along the line of sight from the source to the detector, and not the density itself. There are various ways by which the density variation may be deduced from the absorption measurements. For absorption experiments involving solar observations from rockets or satellites moving through the upper atmosphere, the change in absorption as a function of altitude can be used to determine the density variation. For experiments involving the rising or setting sun, or the occultation of stars, the temporal behavior of the absorption can be used to deduce the density variation as a function of altitude.

The range of altitudes in the upper atmosphere over which continuous absorption experiments will be useful, and the particular atmospheric species that they will be sensitive to, will depend on the

wavelength region used. In general, if a wavelength is selected which is absorbed by only one constituent, its concentration can be accurately determined for a range of about plus or minus one scale height above and below the altitude of unit optical depth.⁽⁹⁾

For wavelengths between 1000 \AA and 2000 \AA the dominant absorbing species is molecular oxygen, so that absorption measurements in this spectral region will be useful in determining the O_2 concentration. If the region between 1400 \AA and 1500 \AA , corresponding to $\sigma_v \sim 10^{-17} \text{ cm}^2$, is used, for example, the O_2 concentration can be studied in the region from about 100 to 120 km. Absorption measurements in the 1650 \AA to 1750 \AA region, where $\sigma_v \sim 10^{-18} \text{ cm}^2$, will determine the O_2 concentration between about 90 and 110 km. If a narrow spectral region around 1216 \AA is chosen, corresponding to the solar Lyman - α line and to an O_2 "window" with $\sigma_v \sim 10^{-20} \text{ cm}^2$, the O_2 concentration in the 70 to 90 km region can be determined.

In the same manner, absorption measurements in the 500 \AA to 1000 \AA region can be used to study the O and N_2 concentrations in the 100 to 200 km region. Absorption experiments in the soft x-ray region, 10 \AA to 100 \AA , can be used to determine the total air density in the 100 to 200 km region. Finally, absorption experiments in the 2000 \AA to 3000 \AA region, where ozone is the dominant absorbing species, can be used to study the ozone layers around 30 to 40 km.

The above discussion pertains to continuous absorption processes. The analysis of line absorption measurements is more complicated due to the rapid variation of the absorption cross section with frequency. It is still true that Beer's law holds for the monochromatic components of the absorption line. However, the experimental wavelength resolution

is usually much broader than the width of the absorption line, so what is measured is not the absorption in one monochromatic piece of the line, but rather the integrated absorption over the entire line. This will be given by the integral of Beer's law over the line profile.

The amount of absorption measured in a spectral line is usually expressed in terms of the equivalent width, W . This is defined as the width of a completely absorbing line which would have the same total absorption as the actual line. In frequency units W is given by

$$W_\nu = \int \frac{I_{0\nu} - I_\nu}{I_{0\nu}} d\nu$$

or

$$W_\nu = \int (1 - e^{-\sigma_\nu \eta}) d\nu$$

where the integral extends over the entire line profile. The equivalent width in wavelength units is $W_\lambda = W_\nu \lambda_0^2 / c$, where λ_0 is the wavelength of the line center.

The calculation of W_ν as a function of η involves a knowledge of the shape of the absorption line as a function of frequency. As we mentioned in Section II, for the upper atmospheric phenomena we are considering, the line shape will be determined by the Doppler broadening and the natural line broadening. The Doppler broadening will determine the shape of the central region of the line, and the natural broadening will determine the shape of the wings of the line.

The behavior of W_ν as a function of η is known as a curve of growth. For the case of combined Doppler and natural broadening, the calculation of the curve of growth is complicated and must be carried out numerically. Reference 10 gives a detailed discussion of the calculation of curves

of growth. Here we will merely note the form of the curve of growth in two limiting cases: For a weak line, where $\sigma_v \eta \ll 1$ over the entire line, the dominant absorption occurs in the center of the line where the Doppler effect is dominant, and W_v is given by

$$W_v = \frac{\pi e^2}{mc} f \eta$$

For a strong line, where the line center is saturated (i.e., $\sigma_0 \eta \gg 1$), appreciable absorption comes from the wings where natural broadening is important, and W_v is given by

$$W_v = \left(\frac{e^2}{mc} f \eta \gamma \right)^{1/2}$$

We see that in these two limiting cases W_v does not depend on Δv_D . However, in the general case the value of W_v will depend on Δv_D .⁽¹⁰⁾

The dependence of W_v on Δv_D complicates the interpretation of line absorption measurements, since it implies that the exact relationship between W_v and η is temperature dependent. Because of this temperature dependence, in order to deduce the value of η from a measurement of W_v , one must have an independent means of determining (or guessing) the value of T .

We see from the above discussion that, as for the case for continuous absorption, line absorption measurements determine η , the total number of absorbing atoms (or molecules) per unit area in the absorbing column, and not the density itself. The density as a function of altitude may be determined by the same techniques discussed for continuous absorption.

Line absorption measurements may be used over a wide range of altitudes in the upper atmosphere. The strongest ultraviolet atomic lines, with absorption cross sections of the order of 10^{-12} cm^2 , may be used to study the density distribution of the atomic constituents (O, N, He, H) up to altitudes of 1000 km or more. The weaker, partially forbidden atomic lines, with cross sections as small as 10^{-17} cm^2 or less, may be used to extend the study of densities down to altitudes of the order of 100 km. The strong absorption lines of the ionized species (O^+ , N^+) will be useful in studying the positive ion concentrations in the ionosphere.

If the sun is used as the source for a line absorption measurement, the details of the solar spectrum must be considered in choosing the spectral line to observe. Above about 2000 \AA the solar spectrum is continuous, with numerous absorption lines (Fraunhofer lines). Below 2000 \AA however, the continuum becomes very weak, and numerous emission lines appear, so that the vacuum ultraviolet solar spectrum is primarily a bright line spectrum. Fortunately for studies of the upper atmosphere, most of the vacuum ultraviolet absorption lines of the atmospheric constituents correspond to strong solar emission lines, so that the details of the solar spectrum do not unduly restrict the number of available absorption lines. For further details concerning the solar ultraviolet spectrum, see Ref. 11.

There have already been a number of absorption studies of the upper atmosphere. Reference 9 presents a discussion of these and further references.

RESONANCE AND FLUORESCENT SCATTERING OBSERVATIONS

Resonance and fluorescent scattering experiments are part of a broader class of spectroscopic observations of the upper atmosphere, all of which involve observations, from above the atmosphere, of the solar ultraviolet radiation reflected by the upper atmosphere, or, in other words, measurements of the ultraviolet dayglow spectrum of the earth. In general, if an arbitrary wavelength region is chosen for such an observation, the reflected radiation observed will be due primarily to Rayleigh scattering, and will not be very sensitive to the atmospheric composition. However, if a wavelength is chosen which coincides with a strong resonance or fluorescent line of some atomic or molecular constituent of the upper atmosphere, the reflected radiation will be due primarily to resonance or fluorescent scattering, and will be a sensitive measure of the distribution of that particular atomic or molecular constituent.

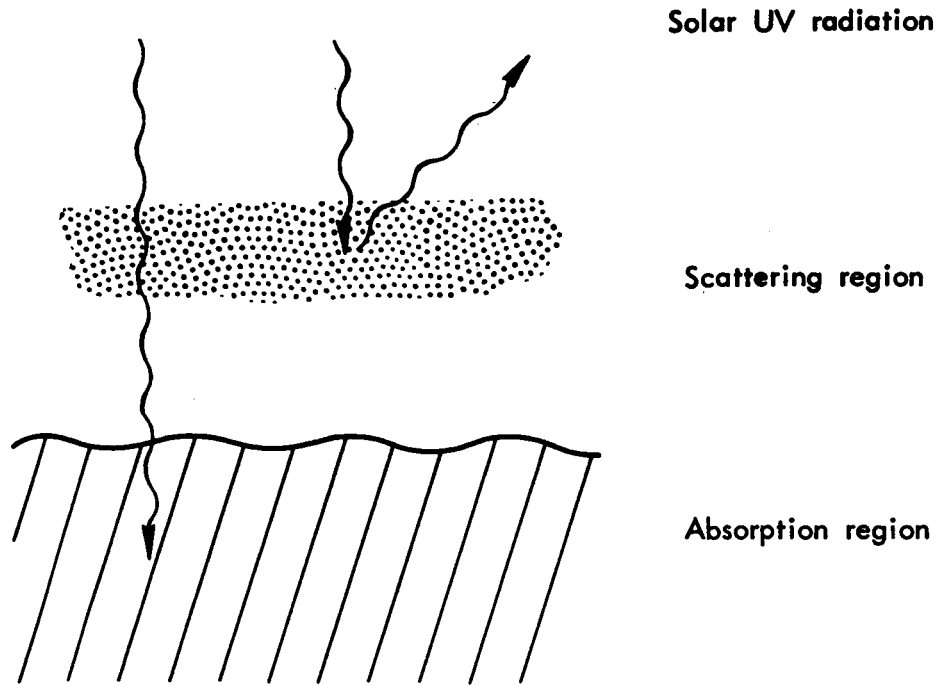
In relating the amount of reflected radiation to the distribution of the scattering constituent, not only single photon scattering, but also the effects of multiple scattering and continuous absorption must be included. In addition, since the width of the spectral line will in general be much less than the instrumental width, we must integrate over the spectral line profile, taking into account the effects of natural broadening and Doppler broadening. The theory of resonance and fluorescent scattering in the upper atmosphere, including the above mentioned effects and using Chandrasekhar's radiative transfer techniques,⁽¹²⁾ has recently been discussed by Chamberlain and Sobouti.^(13,14) The reader is referred to their papers for the theoretical details; here we will only discuss what information concerning the atmospheric

constituents can be obtained from these resonance and fluorescence measurements.

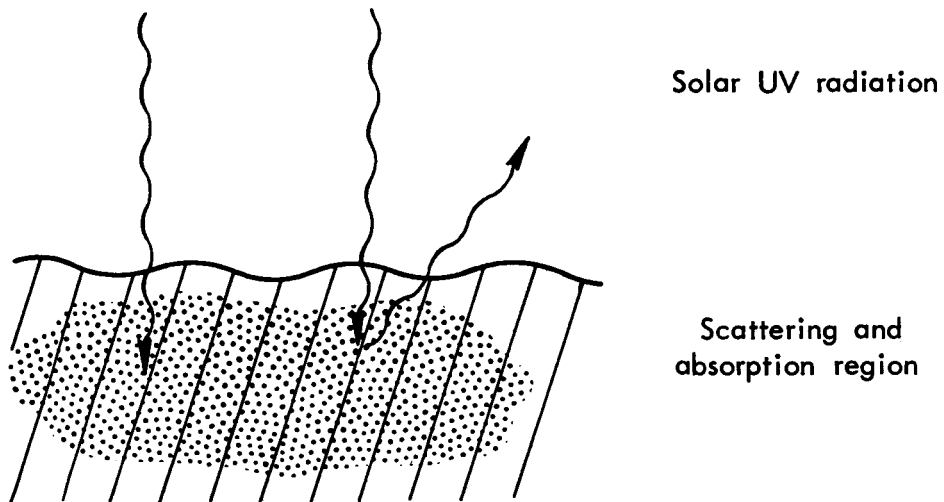
As Chamberlain and Sobouti have shown, it is useful to distinguish between two different cases in discussing the interpretation of resonance and fluorescence measurements in the ultraviolet. The distinction concerns the altitude of the scattering region in the atmosphere relative to the altitude of the absorption region for the particular wavelength of the solar UV spectrum under consideration. The two cases of interest here correspond to: (A) the scattering occurring in a region of the atmosphere above the absorption region, or (B) the scattering occurring in the same altitude region as the absorption (Fig. 3A and 3B).

In the first case (Fig. 3A), the scattering occurring above the absorption region, Chamberlain and Sobouti show that the amount of reflected radiation can be used to determine the total optical thickness of the scattering region at the center of the spectral line, or in other words, the total number of scattering atoms or molecules per unit area above the absorption region. Some examples of this case are:

- (1) The second negative bands of O_2^+ , in the region around 2500 Å. Measurements of the reflected solar radiation in these bands will determine the total amount of O_2^+ above the ozone layer.
- (2) The second negative bands of N_2^+ , in the region around 1500 Å, and the Miescher-Baer bands of NO^+ , in the region around 1400 Å. Measurements of these bands will determine the total N_2^+ and NO^+ concentration above about 120 km, where the O_2 absorption becomes important.



Case A — Scattering occurring above absorption region



Case B — Scattering occurring in absorption region

Fig. 3 — Scattering and absorption regions

- (3) The NII resonance line at 1085 Å and the OII resonance line at 834 Å. Measurements of the resonance scattering in these spectral lines will determine the total N^+ and O^+ concentrations above about 100 km.
- (4) The HI resonance line (Lyman - α) at 1216 Å, the HeI resonance line at 584 Å, and the HeII resonance line at 304 Å. Measurements of the resonance scattering in these spectral lines will determine the total H concentration above about 80 km, and the He and He^+ concentration above about 130 km.
- (5) The OI resonance lines at 1302, 1305 and 1306 Å. Measurements of the reflected radiation from any one of these lines will determine the total neutral oxygen concentration above about 100 km.
- (6) The Herzberg bands of O_2 in the region 2400 Å to 2600 Å. Measurements of the reflected solar radiation in these bands will determine the total amount of O_2 above the ozone layer.

In the second case of interest here (Fig. 3B), where the scattering and absorption occur in the same altitude region, Chamberlain and Sobouti show that the amount of reflected radiation can be used to determine the albedo for single scattering. This in turn determines the ratio of the density of the scattering constituent to the density of the absorbing constituent in the altitude region in question. Some examples are:

- (1) The OI resonance lines at 1355 and 1358 Å. These spectral lines correspond to partially forbidden transitions, and as a result the resonance scattering

cross section for these lines is about 10^{-5} that of the $1302\text{-}1306\text{ \AA}^{\circ}\text{OI}$ multiplet mentioned above. Because of this, the scattering in these lines does not occur high in the atmosphere above the O_2 absorption region, but instead occurs at the same level as the O_2 absorption. Measurements of these lines will therefore determine the O/O_2 ratio in the region around 100 to 120 km.

- (2) The Lyman-Birge-Hopfield bands of N_2 in the region from 1450 \AA° to 1000 \AA° . Measurements of the reflected radiation in these bands will determine the N_2/O_2 ratio in the region around 100 km. (According to Sobouti,⁽¹⁴⁾ these bands may be too weak to be detected in the earth's atmosphere.)

At the present time it is uncertain to which of the above two cases the ultraviolet spectral lines of atomic nitrogen will correspond. This uncertainty is due to our almost complete lack of knowledge of the distribution of atomic nitrogen in the upper atmosphere. However, as pointed out by Chamberlain and Sobouti, the angular distribution of the reflected radiation is distinctly different in the two cases, and this difference can be used to determine the relative location of the scattering and absorption regions for the NI spectral lines. Once this is determined, the interpretation of the NI measurements will be similar to those discussed above.

As seen from the above discussion, certain of the resonance scattering observations may be used to determine the ratios of various species in the upper atmosphere. The significance of the ratios of various species above 100 km to the dynamics of the upper atmosphere

should be emphasized. It is now generally recognized that above 100 to 110 km the atmosphere is in diffusive equilibrium, and that the region of diffusive equilibrium responds quickly (in a few day's time) to changes in composition at its lower boundary.⁽¹⁵⁾ Furthermore, advection, vertical motion, and perhaps tidal or gravity oscillations, play an important part in determining the relative abundances at 100 km of O/O_2 , to a lesser extent that of N_2/O_2 , and possibly of some of the minor constituents as well. Thus, it seems probable that monitoring the O/O_2 ratio above 100 km would provide an indication of the circulation regime below 100 km. There is already some evidence for this interaction between the upper and middle atmosphere^(16,17) and its significance to measurements of composition should not be overlooked. The kind of "synoptic" measurements obtainable from a satellite would be especially valuable in this context.

EMISSION OBSERVATIONS

The study of the emission spectra of the atmosphere in the infrared, visible and near ultraviolet has been actively pursued for a great number of years.⁽⁵⁾ This study has resulted in many significant findings concerning the types of chemical reactions that occur in the atmosphere, the excitation processes responsible for auroras, and the distribution of various of the atmospheric species. With the extension of the spectral coverage of the upper atmosphere to include the middle and vacuum ultraviolet, it is to be expected that emission processes will be found to be important in this region also, and that their study will lead to many important results.

As discussed in Section II, there are a number of photochemical reactions expected to occur in the upper atmosphere which will produce radiation in the middle and vacuum ultraviolet. Since the amount of radiation produced will depend on the concentrations of the reacting species, observations of this radiation (ultraviolet airglow) can be used to study the concentrations of various atomic and molecular species in the upper atmosphere. As one example of this, observations of the radiative recombination reaction



could be used to study the atomic nitrogen distribution high in the atmosphere. At the present time, however, our knowledge of the rate constants for this and other photochemical reactions is very meager. Therefore we could not at the present time unambiguously correlate radiation measurements with species concentration. What is more important, we cannot even estimate the order of magnitude of the radiation to be expected from the various photochemical reactions. Because of this, we do not know which of the photochemical reactions will be most important in the various regions of the ultraviolet spectrum, and we do not know how the amount of radiation from such emission processes will compare with the amount of scattered solar radiation, i.e., we do not know which, if any, of the emission processes will be observable under daylight conditions.

Because of the various uncertainties mentioned above, it is not possible at the present time to outline a definite procedure by which measurements of the middle and vacuum ultraviolet airglow could

be used to provide information concerning conditions in the upper atmosphere. However, based on our experience with airglow research at wavelengths above 3000 \AA , it is safe to say that as our knowledge of this new spectral region increases, we should be able to learn a great deal from the study of the atmospheric emission spectra in the middle and vacuum ultraviolet.

In addition to the radiation from photochemical reactions discussed above, there is also the possibility of radiation due to collisional excitation. As mentioned in Section II, this is expected to be an important source of ultraviolet radiation in auroral regions. Based on our present knowledge of auroral excitation processes and on our experimental knowledge of auroral spectra in the near ultraviolet, visible and infrared, there exist theoretical predictions as to the amount of ultraviolet radiation to be expected from auroras.^(5,18) It would be a very useful check on the understanding of auroral processes to study the auroral spectrum at wavelengths shorter than 3000 \AA , and compare it with the theoretical predictions.

V. PREVIOUS ULTRAVIOLET MEASUREMENTS IN THE UPPER ATMOSPHERE

As indicated earlier, there have already been rocket and satellite observations conducted utilizing some of the techniques discussed here. This section will review these previous experimental studies, briefly describe the nature of the experiments and the instrumentation used, and summarize what was learned from the experiments.

The earliest spectroscopic studies of the upper atmosphere were absorption studies of the general type outlined in Section IV, conducted from rockets and utilizing the sun as the source. These studies, which were an outgrowth of rocket observations of the solar ultraviolet spectrum, have been conducted primarily by the Naval Research Laboratory. Initial results were reported by Friedman,⁽¹⁹⁾ Byram, et al.,^(20,21,22) and Kupperian, et al.,⁽²³⁾ and the work was recently reviewed by Friedman.⁽⁹⁾ The absorption measurements were made using narrow-band photon counters and ion chambers, and the change in absorption as a function of altitude was used to determine the density variation. Thus far, these techniques have been applied to the study of O_2 concentration and total atmospheric density in the upper atmosphere. For the O_2 measurements, photon counters and ionization chambers sensitive to 1060 to 1350 Å, 1225 to 1350 Å, and 1425 to 1500 Å were used to determine the O_2 concentration in the region from 70 to 180 km. For the measurements of atmospheric density, photon counters sensitive to various spectral bands within the 8 to 100 Å region were used, and values of the total atmospheric density were obtained between 100 and 160 km. Reference 9 gives a summary of

the conclusions obtained from these measurements and a detailed discussion of the instrumentation.

A second group of spectroscopic studies of the upper atmosphere consisted of observations of the ultraviolet radiation scattered and emitted by the upper atmosphere. The first of these experiments, conducted by Friedman's group at the Naval Research Laboratory, involved the measurement of the Lyman - α radiation ($1215.7 \overset{\circ}{\text{A}}$) from the atmosphere.^(24,25) The experiment was conducted from a rocket, and used narrow band photon detectors. The daylight albedo of the earth for Lyman - α radiation was found to be 2 per cent. Under nighttime conditions a diffuse Lyman - α glow was found coming from the entire sky (looking up as well as looking down); the apparent nighttime albedo was found to be 42 per cent. It is believed that this Lyman - α radiation from the upper atmosphere is due primarily to resonance scattering, but there may be an emission contribution, and the exact interpretation of the experimental results is still uncertain at the present time.^(9,26)

More recently, other experimental groups have studied the ultraviolet radiation scattered and emitted by the upper atmosphere. Fastie's group at John Hopkins University has used grating spectrophotometers mounted in rockets to study the far ultraviolet spectra of aurora⁽²⁷⁾ and of the day and night airglow.^(28,29) In their auroral observations they have detected emission from several molecular band systems of N_2 and from Lyman - α . In their observations of the day airglow they detected Lyman - α radiation and radiation from the 1302-1305-1306 multiplet of atomic oxygen. In the night airglow they detected only Lyman - α .

Barth and co-workers at the Jet Propulsion Laboratory have used rocket-borne photometers and spectrometers to study the ultraviolet dayglow between 1700 and 3500 Å.⁰ (30,31) Comparison of their results with theoretical calculations of Rayleigh scattering in this spectral region showed that, for the wavelength resolution used in the spectrometer observations, 13 Å,⁰ Rayleigh scattering was much more important than fluorescence scattering.^(31,32)

All of the experiments discussed above employed rockets. The first satellite observations of the ultraviolet spectra of the upper atmosphere have recently been carried out by Friedman, et al.^(33,34) These observations employed photometers with bandwidths of 280 and 520 Å,⁰ centered at 2550 Å,⁰ to measure the background radiance of the earth in the middle ultraviolet. The daytime value averaged over this spectral region was found to be approximately 2×10^{-9} watts/cm²·ster·Å.⁰ No radiation was detected on the dark side of the earth.

A much more extensive study of the ultraviolet spectra of the upper atmosphere will be initiated with the launching of the first POGO (Polar Orbiting Geophysical Observatory) satellite, which is scheduled for 1964. The POGO series of satellites will carry, along with several other types of experiments, a number of photometer and spectrometer experiments to study the middle and vacuum ultraviolet.⁽³⁵⁾

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